(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 0 698 772 A1

(12) EUROPEAN PATENT APPLICATION

(43) Date of publication:
28.02.1996 Bulletin 1996/09

(51) Int Cl.[6]: **F25J 3/04**

(21) Application number: **95305598.5**

(22) Date of filing: **11.08.1995**

(84) Designated Contracting States:
BE DE FR GB IT NL

(30) Priority: **25.08.1994 US 295951**

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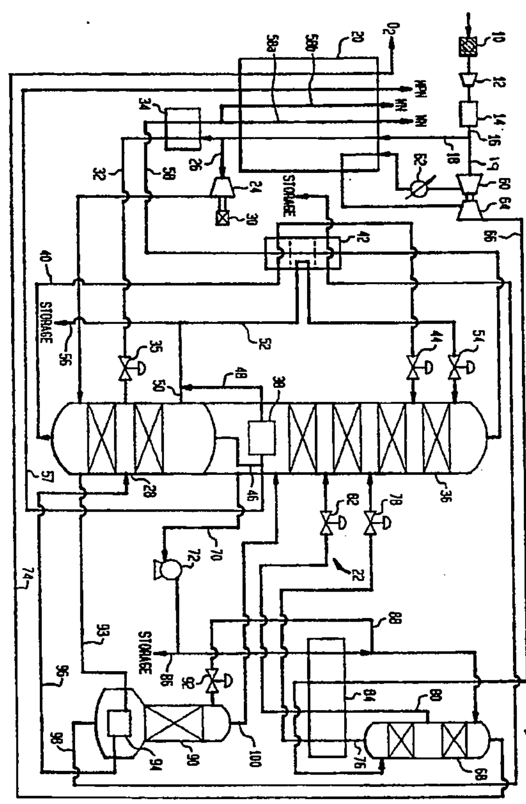
(54) Method and apparatus for producing oxygen

(57) A, filtered, compressed and purified air stream is divided into first and second air streams 18 and 20 respectively. The first air stream is separated by a low temperature rectification process operating in accordance with a Claude cycle to produce liquid oxygen in a lower pressure column 28 of a double column air separation unit. A Claude expander 24 expands at least a major portion of the first air stream into the high pressure column 28. The second air stream 20 is further compressed in a booster-compressor 60, is cooled in a main heat exchanger 20 and is expanded in a turboexpander 64 with the performance of work which is in turn applied to the work of compression of the second air stream. Liquid oxygen is pumped by pump 72 from a lower pressure column 36 to substantially a desired delivery pressure and is vaporized within a mixing column 68 by counter-current contact the second air stream 20 which is also introduced into the mixing column. A liquid stream composed of the liquid produced in the mixing column is introduced into an intermediate location of a lower pressure column 36 to add the refrigeration of the second air stream to the process.



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Description

The present invention relates to a method and apparatus for producing oxygen in which the production is carried out in accordance with a Claude cycle.

Air is conventionally separated by a process that includes cooling a filtered, compressed and purified air stream to a temperature suitable for its rectification. The air stream is introduced into a double column air separation unit employing higher and lower pressure columns. The air is rectified in the higher pressure column to produce at a bottom region thereof an oxygen-enriched liquid and at a top region thereof a nitrogen-rich vapour. The oxygen-enriched liquid is separated in the lower pressure column to produce liquid oxygen and nitrogen. In a Claude cycle, the incoming air stream is compressed to a pressure well above the pressure of the higher pressure column and is turboexpanded upstream of its introduction into the higher pressure column. The turboexpansion of the air adds refrigeration to the process in order to compensate for thermodynamic irreversibility of the process and for heat absorbed from outside the process. Moreover, in a Claude cycle extra refrigeration can be supplied to enable a proportion of the products of the air separation to be produced in liquid state.

If a gaseous oxygen product is to be produced, a stream of the liquid oxygen can be pumped to the delivery pressure. The thus pressurized liquid oxygen stream can be vaporized within the main heat exchanger by heat exchange with a portion of the incoming air stream that has been boosted in pressure. Alternatively, an oxygen compressor can be used to compress a product stream at the warm end of the main heat exchanger.

An advantage of the Claude cycle is that a large proportion of the work of compression can be dedicated to the production of liquid oxygen. A disadvantage is that additional energy is required to compress the incoming air stream above the higher pressure column pressure. This problem is exacerbated when a gaseous oxygen product is formed by pressurising and vaporising a liquid oxygen stream in the main heat exchanger. As will be discussed, the present invention provides a modification in the Claude process so that a gaseous oxygen product can be produced at pressure with a lower expenditure of energy over a prior art Claude process.

It is known to vaporise a pumped liquid oxygen stream by direct heat exchange between it and a higher volatility stream within a mixing column. In operation of a mixing column a less volatile stream is introduced in liquid state at the top thereof, and a more volatile vaporous stream is caused to ascend the mixing column from the bottom thereof. The descending liquid phase and ascending vapour phase are intimately contacted in the mixing column with the result that the vapour phase becomes progressively richer in a less volatile component, and the vapour phase in a more volatile component. If the higher volatility stream is formed of air, gaseous oxygen is produced at the top and liquid air at the bottom of the mixing column.

According to the present invention there is provided a method for producing a gaseous oxygen product at a delivery pressure, comprising:

a) performing a Claude cycle rectification of air which comprises expanding with the performance of work a first compressed, precooled stream of purified air, and separating a stream of the expanded air in a double rectification column comprising a higher pressure rectification column, a lower pressure rectification column, and a condenser-reboiler placing the higher pressure rectification column in heat transfer relationship with the lower pressure rectification column, and obtaining by the separation liquid oxygen in a bottom region of the lower pressure rectification column, the stream of the expanded air being introduced into the higher pressure rectification column;

b) pumping a stream of said liquid oxygen at a chosen pressure into the top region of a mixing column;

c) introducing a supplemental vaporous refrigerant air stream into a bottom region of the mixing column;

d) withdrawing at substantially said delivery pressure a gaseous oxygen stream from the top region of the mixing column; and

e) withdrawing a liquid refrigerant stream from the bottom region of the mixing column and introducing the liquid refrigerant stream into an intermediate location of the lower pressure rectification column.

The present invention also provides apparatus for producing a gaseous oxygen product at a delivery pressure, comprising:

a) at least one compressor for compressing a flow of air;

b) a pre-purification unit for purifying the flow of air;

c) a main heat exchanger for cooling a first stream of the compressed, purified air by heat exchange with returning products of air separation;

d) a double rectification column for separating air comprising a higher pressure rectification column, and a condenser-reboiler placing the higher pressure rectification column in heat transfer relationship with the lower pressure rectification column;

e) a Claude expander for expanding air with the performance of external work having an inlet for the cooled first stream of compressed, purified air and an outlet communicating with the higher pressure

rectification column;

f) means for forming a supplemental vaporous refrigerant air stream at substantially said delivery pressure;

g) a pump communicating with the lower pressure rectification column for withdrawing a stream of liquid oxygen therefrom and for raising the pressure of the stream of liquid oxygen to a delivery pressure;

h) a mixing column having an inlet for the pressurised stream of liquid oxygen at its top region, an inlet at its bottom region for the supplemental vaporous refrigerant air stream, an outlet at its top region communicating with the main heat exchanger for the gaseous oxygen product, and an outlet at its bottom region for a liquid refrigerant stream; and

i) a valve intermediate the outlet for the liquid refrigerant stream and an inlet to the lower pressure rectification column for reducing the pressure of the liquid refrigerant stream.

It is to be noted that in the mixing column, as in any column, there will be a pressure drop from bottom to top of the mixing column. Therefore, the pressure of the supplemental refrigerant stream used to vaporize the liquid oxygen will have a pressure that will be slightly higher than the liquid oxygen pumped pressure.

The term "fully warmed" as used herein means warmed to a temperature of the warm end of a main heat exchanger and the term "fully cooled" means cooled to a temperature of the cold end of the main heat exchanger. The terms "partially warmed" or "partially cooled" mean warmed or cooled, respectively, to a temperature intermediate the warm and cold ends of the main heat exchanger.

The mixing column serves, in effect, as a vaporizer of the stream of the liquid oxygen. As mentioned above, in a Claude cycle there is an energy penalty because most of the air must be compressed above the operating pressure range of the higher pressure column. Equipment and energy costs savings are made possible by the method and apparatus according to the invention through integration of a mixing column with the air separation plant such that a supplemental refrigerant stream is utilized both to vaporize the product stream and to supply a portion of the required plant refrigeration.

If desired, the refrigerant stream can be formed from a portion of the exhaust of the Claude expander. Such an embodiment could be used if the oxygen product is required at or below the pressure of the higher pressure column. Alternatively, an additional expander (i.e. expansion turbine) may be used to form the refrigerant stream.

If desired a booster compressor may be used to compress further the refrigerant stream upstream of its expansion. For example, part of the compressed air stream can be boosted in pressure, partially cooled within the main heat exchanger and expanded by an expander so coupled to the booster compressor that the work of expansion is applied to drive the booster compressor. In such an embodiment the refrigeration requirements for the Claude part of the cycle can be reduced, thus making possible energy savings. A combination of the two embodiments are possible. For instance, when there is a need for liquid production both the booster compressor and additional expander are used to form the refrigerant stream. During periods of low liquid production requirements, the booster compressor is turned off and the refrigerant stream is formed from a portion of the exhaust of the Claude expander.

In a preferred embodiment of the apparatus according to the invention that utilizes a booster compressor, the Claude expander expands approximately 75% of the air. The further expander coupled to the booster compressor produces approximately 40% of the refrigeration utilizing about 23% of the total air. In such case, the Claude expander will produce the additional 60% of the refrigeration. By producing this excess refrigeration in the mixing column, the head pressure in the main air compressor can be lowered. In the foregoing example a head pressure of approximately 9.8 atmospheres absolute produces a 60/40 split of refrigeration between the two expanders. If 100% of the refrigeration had to be produced in a single Claude expansion machine by expanding 100% of the air, the head pressure of the air compressor would have to be increased by approximately 1.5 atmospheres absolute. This in turn would equate to a power difference of approximately 6%. Hence, the method and apparatus according to the invention make possible the effective supply of refrigeration from the mixing column to reduce the work of compression that needs to be performed. Further power savings in the present invention can be realized by coupling the Claude expander to a generator. Other advantages of the present invention will become apparent in a description of a preferred embodiment in accordance with the present invention.

The method and apparatus according to the invention will now be described by way of example with reference to the accompanying drawing which is a schematic process flow diagram of an air separation plant.

Referring to the drawing, in apparatus 1 a flow of air is filtered by a filter 10, is compressed by a compressor 12, and is purified within a prepurification unit 14. Prepurification unit 14 removes contaminants from the air such as carbon dioxide and water that would interfere with the air separation process. As is known in the art, prepurification unit 14 consists of a series of beds of adsorbent operating out of phase for regeneration purposes.

The thus filtered, compressed and purified air stream 16 is divided into first and second air streams 18 and 19. The first air stream 18 is separated by a low temperature rectification process operating in accordance with a Claude cycle. The low temperature rectification

process includes a cooling stage formed by a main heat exchanger 20 for cooling the first air stream 18 to a temperature suitable for its rectification and a double rectification column or air separation unit 22 which acts as a rectification stage to rectify the air into oxygen and nitrogen. A Claude expander 24 expands at least a major portion 26 of first air stream 18 into a higher pressure column 28 of the air separation unit 22. The Claude expander 24 can be a turboexpander which is preferably connected to a generator 30 to recover electrical energy for use in the plant, for instance, operating the main air compressor or connected to a product compressor. An optional minor portion 32 of the air is further cooled within a waste heater 34 which serves to pre-warm a waste nitrogen stream to be discussed hereinafter. Major portion 26 is introduced into the bottom region of higher pressure column 28. Minor portion 32 of air stream 18 downstream of being reduced in pressure by a valve 35 is also introduced into higher pressure column 28. In a possible alternative embodiment in accordance with the present invention, waste heater 34 could be omitted so that all of the first air stream 18 is routed to Claude expander 24.

Air separation unit 22 is also provided with a lower pressure column 36 connected to the higher pressure column 28 in a heat transfer relationship by means of a condenser reboiler 38. Both higher and lower pressure columns 28 and 36, respectively, are provided with liquid-vapour contacting elements, such as trays, structured packing, random packing and the like to bring vapour and liquid phases of the mixture to be separated into intimate contact with one another. In the higher pressure column 28, an oxygen-rich liquid is at the bottom and a nitrogen-rich vapour at the top are produced. An oxygen-rich liquid stream 40, is withdrawn from the bottom of the column 28 and is subcooled within a subcooler 42 and is reduced in pressure to that of the lower pressure column 36 by a pressure reduction valve 44. The reduced pressure oxygen-rich liquid stream 40 is introduced into the lower pressure column 36 for separation into liquid oxygen which collects within a lower sump portion of the lower pressure column 36 and nitrogen vapour at the top of the column 36.

The liquid oxygen is vaporized within the sump of lower pressure column 36 by heat exchange with the condensing nitrogen-rich vapour separated in the higher pressure column 28. This is effected by withdrawing a nitrogen-rich vapour stream 46 and condensing said stream within the condenser/reboiler 38 to form a liquid reflux stream 48. A first portion 50 of liquid reflux stream 48 is introduced into the top region of higher pressure column 28 for reflux purposes. A second portion 52 of reflux stream 48 is subcooled within subcooler unit 42, is reduced in pressure by means of a pressure reduction valve 54 to the pressure of lower pressure column 36 and is introduced into a top region of the lower pressure column 54. A liquid medium pressure nitrogen stream 56 may be taken from the reflux stream 48 and stored. A medium pressure product nitrogen stream 57, formed from part of the nitrogen-rich vapour stream 46, can be fully warmed within main heat exchanger 20 by passage therethrough from its cold end to its warm end.

A waste nitrogen stream 58 is withdrawn from lower pressure column 36 and is warmed within the subcooler unit 42. The warmed waste nitrogen stream 58 is routed through waste heater 34. Waste heater 34 helps raise the temperature of the waste nitrogen stream 58 to that of the other streams to be warmed in the main heat exchanger 20. After passage through waste heater 34, waste nitrogen stream 58 is split into two partial streams 58a and 58b which are fully warmed within main heat exchanger 20 in a countercurrent direction to the incoming air. Downstream of the main heat exchanger 20, the partial stream 58a, which constitutes most of the flow of the waste nitrogen, may be used to cool water. The partial stream 58b can be used in the regeneration of the prepurification unit 14. This division of flow in the waste nitrogen allows main heat exchanger 20 to be designed with a lower overall waste stream pressure drop because the water cooler typically operates with a lower pressure drop than the prepurification unit 14.

The Claude expander 24 supplies part of the refrigeration requirements of apparatus 1. The remainder of the refrigeration requirements are supplied by a turboexpander the second air stream 20 is compressed within a booster compressor 60. Downstream of removal of the heat of compression by an aftercooler 62, the compressed second air stream 20 is partially cooled within main heat exchanger 20 and expanded within the turboexpander 64. The turboexpander 64 performs work of expansion which is applied to booster-compressor 60 preferably through a mechanical linkage. The second air stream 19 and taken from the turboexpander 64 as a supplemental refrigerant stream 66.

The supplemental refrigerant stream 66 has substantially the delivery pressure that is required for the gaseous oxygen product and is introduced into a mixing column 68. At the same time, a liquid oxygen stream 70 is removed from the bottom of lower pressure column 36 and pumped by a pump 72 to substantially the delivery pressure. The pressurised liquid oxygen stream 70 is introduced into a top region of mixing column 68. The mixing column, which has liquid-vapour contacting elements such as packing or trays (e.g. sieve trays), functions as a direct heat exchanger to vaporize the liquid oxygen and to produce a gaseous oxygen product in the top region of mixing column 68. The gaseous oxygen product (which will contain some impurity as a result of the liquid-vapour contact between descending liquid and ascending vapour in the mixing column 68) is removed as a product stream 74, which is warmed within the main heat exchanger 20. The gaseous oxygen product typically contains 95 mole per cent of oxygen. Liquid oxygen is removed as a liquid stream 76, which downstream of pressure reduction by a valve 78, is introduced into the lower pressure column 36 to apply further refrigeration to the process. An intermediate liquid stream 80 can also

be removed from the mixing column 68 and introduced into the lower pressure column 36 downstream pressure reduction in a valve 82 in order to maintain the thermal efficiency of mixing column 68.

Since the pressurised liquid oxygen stream 70 is typically in a subcooled state, the liquid oxygen stream 70 is warmed within a subcooling heat exchanger 84 upstream of its introduction into mixing column 68. The warming is effected by countercurrent heat exchange with refrigerant stream 66, liquid refrigerant stream 76 and intermediate liquid stream 80.

If desired, the apparatus 1 may be arranged so as to permit its operation even when the booster-compressor 60 and the turboexpander 64 are deactivated. In this example, a valved branch line (not illustrated) is provided between the Claude expander 24 and the bottom region of mixing column 68 to divert some of the flow from the higher pressure column 28 to the mixing column 68. The diverted flow would constitute the supplemental refrigerant stream during such operation of apparatus 1. As a consequence, the rate of producing liquid oxygen product would be reduced.

Optionally, a pressurized liquid oxygen stream 86 can be withdrawn upstream of the heat exchanger 84 and passed to storage. Also as another option, an auxiliary liquid stream 88 can be removed either upstream of (not shown) or downstream of the heat exchanger 84 and introduced into the top of a high purity scrubbing column 90 which operates at a pressure not less than that of the lower pressure column 36. If scrubbing column 90 were operated at a higher pressure than the lower pressure column 36, a pressure reduction valve (not shown) is provided. Since the high purity scrubbing column 90 typically operates at a pressure below mixing column 68, the auxiliary liquid stream 88 is reduced in pressure by passage through a valve 92. Reboil for the column 90 is provided by removing a gaseous air stream 93 from the column 28 and condensing the gaseous air contained within a condenser/reboiler 94 located in the bottom of the column 90. Liquid stream 96 is returned to the higher pressure column 28. As a result, the liquid oxygen is scrubbed by rising vapour to produce a high purity liquid oxygen fraction relatively free of argon impurity at the bottom which is withdrawn as an auxiliary product stream 98. The auxiliary product stream 98 is sent through subcooler 42 and then to storage. A stream of vapour 100 is returned from the column 90 to the lower pressure column 36.

Claims

1. A method for producing a gaseous oxygen product at a delivery pressure, comprising:

   a) performing a Claude cycle rectification of air which comprises expanding with the performance of work a first compressed, precooled stream of purified air, and separating a stream of the expanded air in a double rectification column comprising a higher pressure rectification column, a lower pressure rectification column, and a condenser-reboiler placing the higher pressure rectification column in heat transfer relationship with the lower pressure rectification column, and obtaining by the separation liquid oxygen in a bottom region of the lower pressure rectification column, the stream of the expanded air being introduced into the higher pressure rectification column;

   b) pumping a stream of said liquid oxygen at a chosen pressure into the top region of a mixing column;

   c) introducing a supplemental vaporous refrigerant air stream into a bottom region of the mixing column;

   d) withdrawing at substantially said delivery pressure a gaseous oxygen stream from the top region of the mixing column; and

   e) withdrawing a liquid refrigerant stream from the bottom region of the mixing column and introducing the liquid refrigerant stream into an intermediate location of the lower pressure rectification column.

2. A method according to claim 1, in which the supplemental, vaporous, air stream is formed at its chosen pressure by expanding with the performance of external work a second compressed, precooled stream of purified air.

3. A method according to claim 1 or claim 2, additionally including the step of warming the stream of liquid oxygen to its saturation temperature at the chosen pressure, the warming being performed by heat exchange with the second air stream.

4. A method according to any one of claims 1 to 3, additionally including the step of taking a liquid oxygen product from the lower pressure rectification column.

5. A method according to any one of the preceding claims, additionally including the steps of purifying a further stream of said liquid oxygen in a stripping column, reboiling liquid in a bottom region of the stripping column by indirect heat exchange with a further air stream, the further air stream thereby being condensed, introducing the resulting condensed air stream into the higher pressure rectification column, withdrawing a purified liquid oxygen product from the stripping column, and introducing

a vapour stream taken from the top of the stripping column into the lower pressure rectification column.

6. A method according to any one of the preceding claims, additionally including the steps of withdrawing an intermediate liquid stream from an intermediate region of the mixing column, reducing the pressure of the intermediate liquid stream, and introducing it into the lower pressure rectification column.

7. A method according to any one of the preceding claims, further comprising recovering the work of expansion from the Claude expander as electrical energy.

8. Apparatus for producing a gaseous oxygen product at a delivery pressure, comprising:

a) at least one compressor for compressing a flow of air;

b) a pre-purification unit for purifying the flow of air;

c) a main heat exchanger for cooling a first stream of the compressed, purified air by heat exchange with returning products of air separation;

d) a double rectification column for separating air comprising a higher pressure rectification column, and a condenser-reboiler placing the higher pressure rectification column in heat transfer relationship with the lower pressure rectification column;

e) a Claude expander for expanding air with the performance of external work having an inlet for the cooled first stream of compressed, purified air and an outlet communicating with the higher pressure rectification column;

f) means for forming a supplemental vaporous refrigerant air stream at substantially said delivery pressure;

g) a pump communicating with the lower pressure rectification column for withdrawing a stream of liquid oxygen therefrom and for raising the pressure of the stream of liquid oxygen to a delivery pressure;

h) a mixing column having an inlet for the pressurised stream of liquid oxygen at its top region, an inlet at its bottom region for the supplemental vaporous refrigerant air stream, an outlet at its top region communicating with the main heat exchanger for the gaseous oxygen product, and an outlet at its bottom region for a liquid refrigerant stream; and

i) a valve intermediate the outlet for the liquid refrigerant stream and an inlet to the lower pressure rectification column for reducing the pressure of the liquid refrigerant stream.

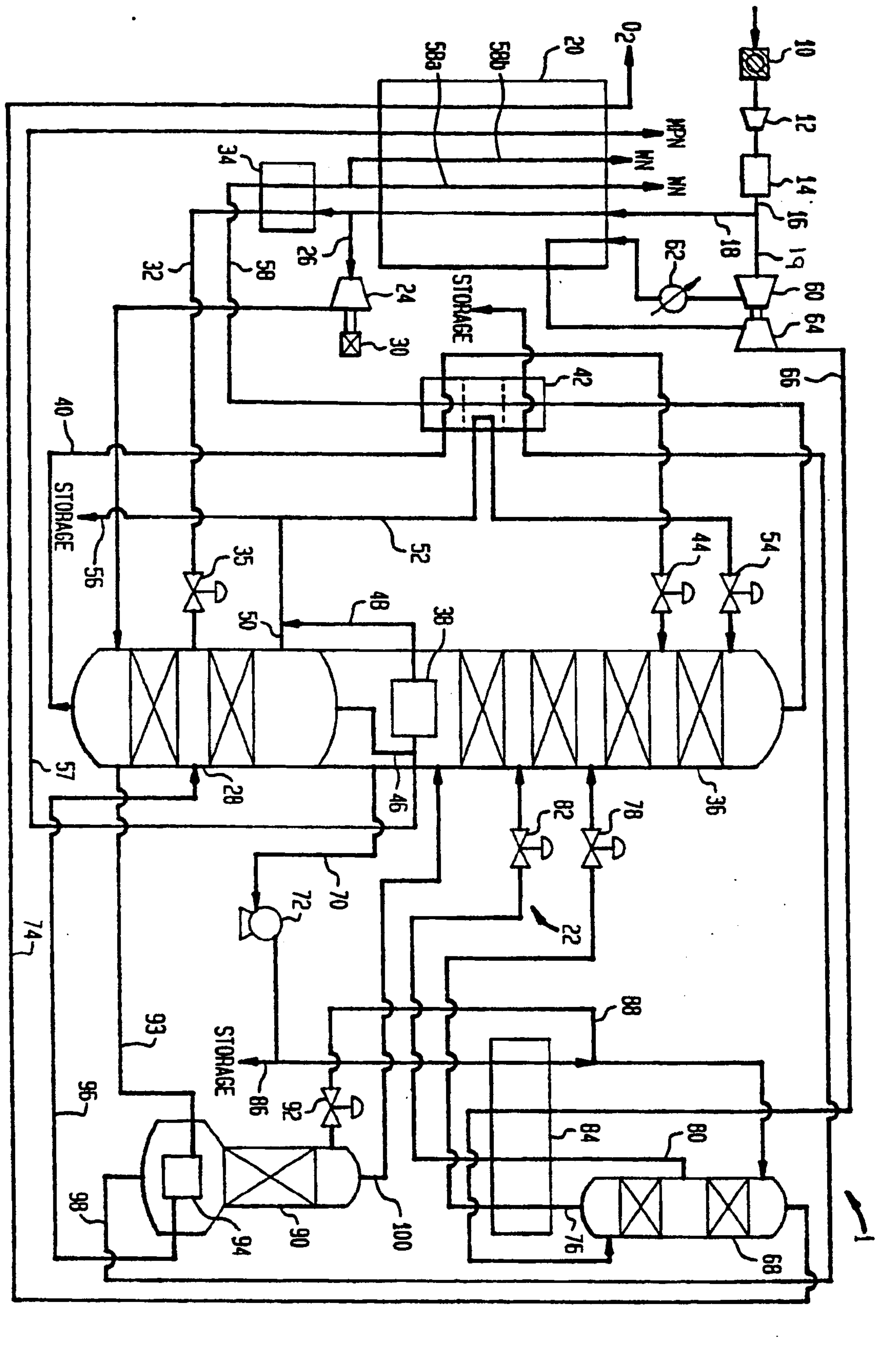
9. Apparatus according to claim 8, wherein the means for forming the supplemental vaporous refrigerant air stream comprises a second expander for expanding a second stream of air with the performance of external work.

10. Apparatus according to claim 9, additionally including a further heat exchanger for warming the stream of liquid oxygen to its saturation temperature.

11. Apparatus according to any one of claims 8 to 10, additionally including an outlet from the apparatus for a liquid oxygen product communicating with the lower pressure rectification column.

12. Apparatus according to any one of claims 7 to 9, additionally including a stripper column for purifying a further stream of pressurised liquid oxygen, the stripper column having an inlet for the liquid oxygen communicating with an outlet of the pump.

13. Apparatus according to any one of claims 7 to 10, wherein the mixing column has at an intermediate level thereof an outlet for an intermediate liquid refrigerant stream communicating via a pressure reducing valve with the lower pressure rectification column.



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EUROPEAN SEARCH REPORT

Application Number
EP 95 30 5598

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
X	DE-A-42 19 160 (L'AIR LIQUIDE) * claims 1,2,6,7; figure 2 *	1-4, 6-11,13	F25J3/04
A	EP-A-0 531 182 (L'AIR LIQUIDE) * claims; figures *	1-13	
X,P	EP-A-0 636 845 (BOC) * claims; figure 4 *	1-13	

TECHNICAL FIELDS SEARCHED (Int.Cl.6)

F25J

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	9 November 1995	Meertens, J

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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